(12) **UK Patent Application** (19) **GB** (11) **2 236 402** (13) **A**

(43) Date of A publication 03.04.1991

(21) Application No 8920403.6

(22) Date of filing 08.09.1989

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(51) INT CL⁵
G02F 1/35

(52) UK CL (Edition K)
G2F FCW F23E F25M2 F28W

(56) Documents cited
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(58) Field of search
UK CL (Edition J) G2F FCW
INT CL⁴ G02F
Online database WPI

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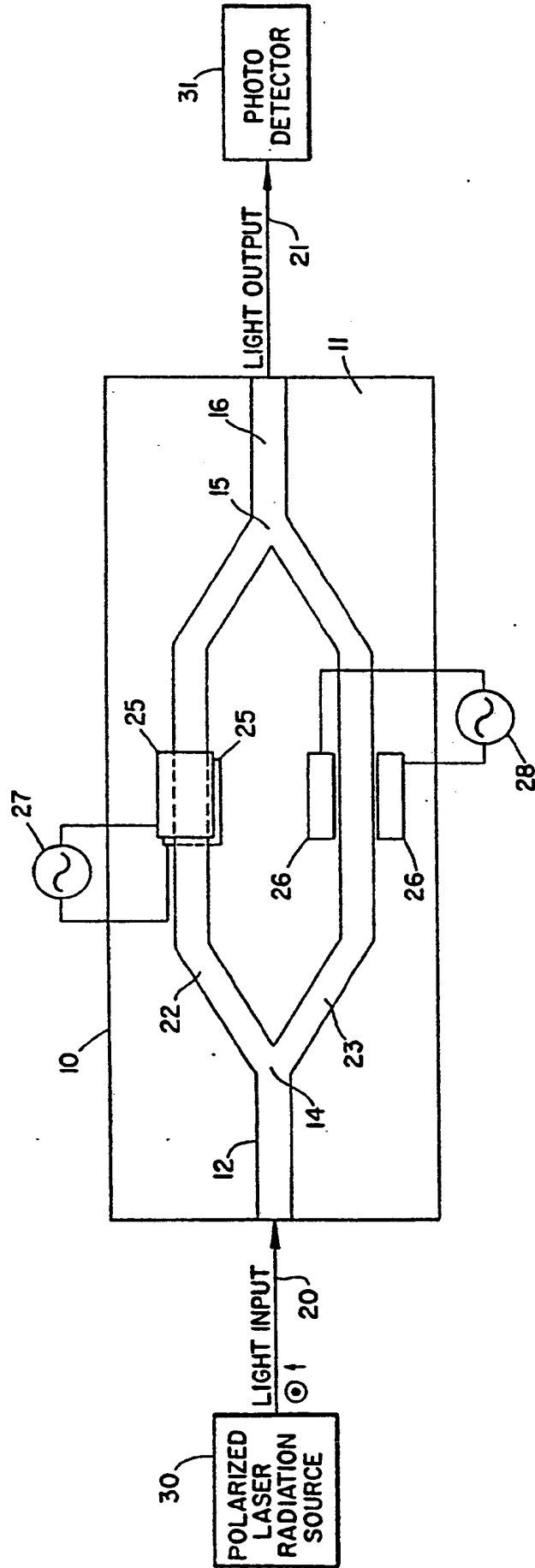Chelmsford, Essex, CM2 8HN, United Kingdom**

(54) **Electro-optic waveguide device**

(57) An electro-optic waveguide device, e.g. radiofrequency optical modulator of the Mach-Zehnder interferometer configuration, is provided with polymeric cladding layers which are formed of the same general type of electro-optic polymer as the waveguiding region. The waveguide region and/or cladding is a polymer which exhibits second order nonlinear optical susceptibility or contains an organic compound having such properties.

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This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

Fig.1

POLARIZATION-INSENSITIVE MACH-ZEHNDER MODULATOR

⊙ TE mode
↑ TM mode

Fig.2

Fig.3

43 44 41

Fig. 4

45 42 A 46

2A 44 42C 42

B 42B B 43
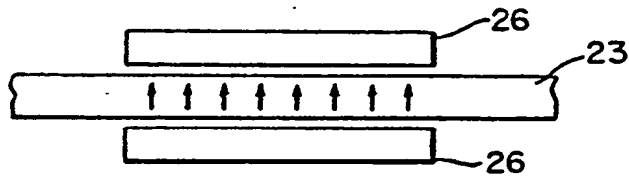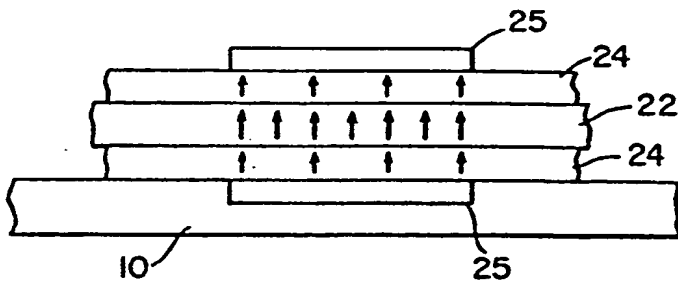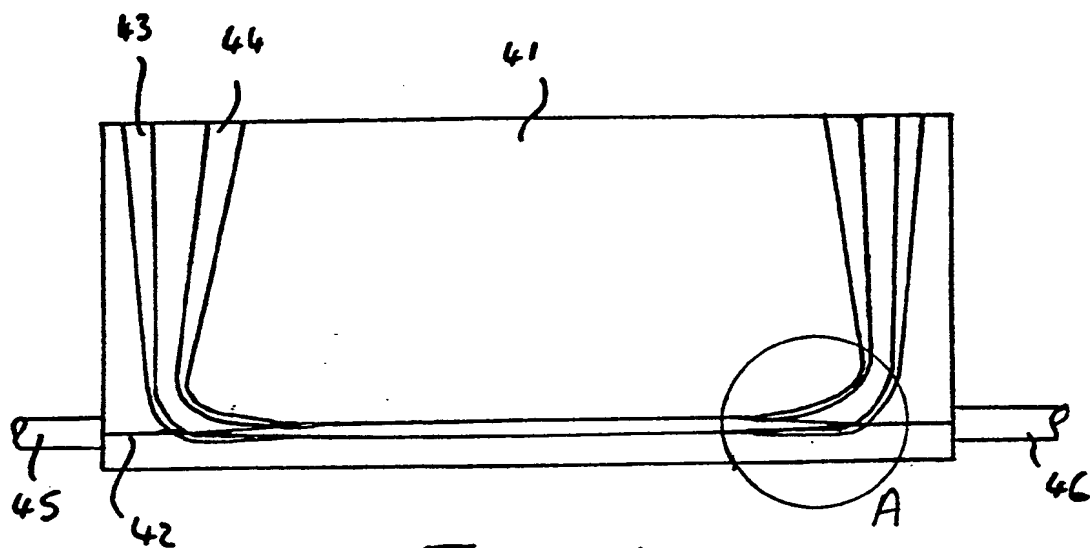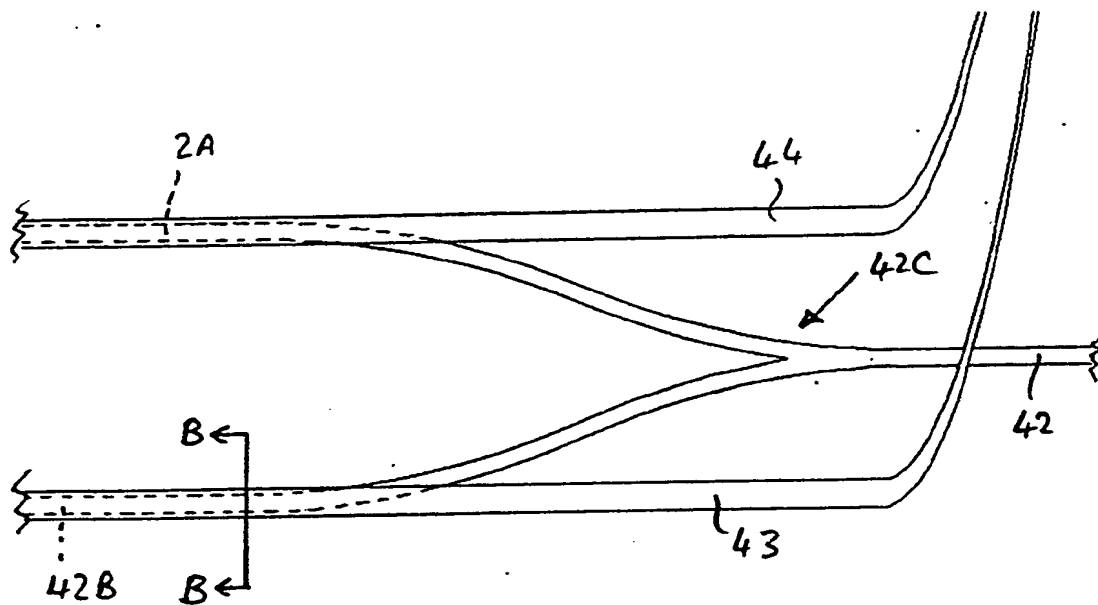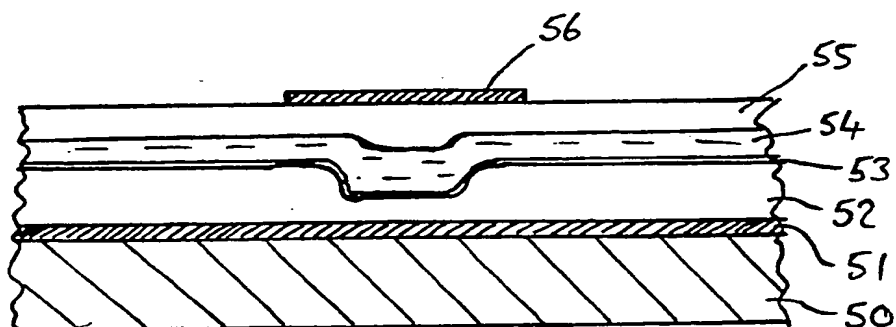
Fig. 5

Fig. 6

ELECTRO-OPTIC WAVEGUIDE DEVICE

This invention relates to an electro-optic waveguide device, and in particular to a device of the type having polymeric electro-optic waveguiding region.

Such a device may serve, for example, as a modulator for use in a radio frequency fibre optic link. Light, for example from a semi-conductor laser, is passed along the waveguiding region and is phase modulated by a radio frequency signal applied to electrodes extending parallel to the waveguide. Since, in any r.f. fibre optic link, significant losses of signal are obtained in the conversion of the r.f. signal to an optical signal and then back to an r.f. signal, there is a link length below which conventional co-axial cables, although subject to high signal loss per unit length, offer a lower loss than the corresponding fibre optic link. It is therefore desirable in fibre optics to minimise the losses in conversion of the r.f. signal to an optical signal.

The use of polymeric electro-optic materials in integrated optic modulators and other electro-optic

waveguide devices offers significant advantages over conventional inorganic electro-optic crystals, such as lithium niobate. The characteristics of the materials themselves may be superior, and the fabrication of waveguides is greatly simplified. Further, there are certain inherent disadvantages in the use of inorganic crystal materials such as lithium niobate in an electro-optic modulator, for example the limitation of the input optical power because of the inherent photo-refractive effect, and the high fabrication cost for a high quality lithium niobate or like crystal.

It is known that organic, particularly polymeric, materials with large de-localised pi-electron systems can exhibit a non-linear optical response, which is in many cases much larger than in inorganic substrates. Additionally, the properties of organic materials can be varied to optimise other desirable properties, such as mechanical and thermal stability and laser damage threshold, while preserving the electronic interactions responsible for non-linear optical effects. Of particular importance for conjugated organic systems is the fact that the origin of the non-linear effects is the polarisation of the pi-electron cloud as opposed to the displacement or re-arrangement of nuclear

co-ordinates found in inorganic materials. Organic
non-linear optical media in the form of transparent thin
substrates are described in US Patents 4 536 450, 4 605
869, 4 607 095, 4 615 962, and 4 624 872. Additionally,
a symposium sponsored by the Polymer Chemistry Division
of the American Chemical Society at its 18th Meeting in
September 1982 was concerned with "Non-linear Optical
Properties of Organic and Polymeric Materials", and
papers presented on this subject at the meeting were
published in ACS Symposium Series 233 by the American
Chemical Society, Washington D.C., in 1983.

To avoid excessive loss arising from the
interaction of the guided optical wave with the metallic
electrodes which apply the electric field to the
elctro-optic waveguiding region, buffer or cladding
layers of transparent material having a refractive index
lower than that of the waveguide are employed. The
buffer layers are interposed between the electrodes and
the electro-optic waveguide. However, the buffer layers
reduce the electric field in the waveguide for a fixed
bias, or higher voltages are required for a fixed field.
A trade-off between optical loss and drive voltage
therefore determines the optimum buffer layer thickness.

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Device length is another relevant variable, since loss is proportional to length and the required voltage is inversely proportional to length. Hence, a device with thick buffer layers and low loss per unit length may be optimised at a longer total length to give the best combinations of drive voltage and total loss.

Moreover, the thickness of the buffer layers required is a function of the refractive index of the buffer and that of the waveguide, and also of the polarisation of the optical beam. Deriving the optimum trade-off also involves a knowledge of the electro-optic co-efficient of the guide, optical scattering losses, microwave electrode losses, and a number of mechanical application and economic constraints. An optimum buffer layer choice can be compromised if layer thicknesses or material properties change as a result of process fluctuations.

These trade-offs and compromises, together with the loss of voltage sensitivity, are avoided by the use, in accordance with the present invention, of buffer or cladding layers which are electro-optic, like the waveguide. According to the present invention, an electro-optic waveguide device comprises a polymeric

electro-optic waveguiding region located between upper and lower cladding layers of lower refractive index than the waveguiding region, and electrodes for applying an electric field to the waveguiding region, at least one of the cladding layers being an electro-optic layer. Preferably both cladding layers are electro-optic layers.

The waveguiding region may be defined in a channel in a substrate material or, in another embodiment, as a rib on the surface of the substrate. In each case, one of the cladding layers will also tend to extend over at least a part of each side of the waveguiding region.

The polymeric material from which the waveguiding region and/or the cladding layers are formed may comprise a polymeric host matrix and an organic guest compound which exhibits second order non-linear optical susceptibility. Alternatively, the layers may comprise an organic polymer with pendent side chains which exhibit second order non-linear optical susceptibility.

The waveguiding region may be a region having stable electric field-induced non-centrosymmetric polymolecular orientation, i.e. a poled region. The

cladding layers may also have stable electric field-induced zones of non-centrosymmetric polymolecular orientation. Such zones may be formed at the same time as poling of the waveguiding region.

The waveguiding region and the cladding layers may each comprise a compound containing a stilbene structure in conjugation with an electron donating group and an electron withdrawing group. For example, the layers may each comprise an acrylic co-polymer with pendent side chains which contain a 4-amino-4'-nitrostilbene structure.

The cladding layers suitably each have a refractive index 0.001 to 0.2 lower than the waveguiding region.

The invention also provides a radiofrequency optical modulator comprising an optical waveguide structure arranged as a Mach-Zehnder interferometer, wherein each branch of the interferometer is formed of a polymeric electro-optic material having a stable electric field-induced noncentrosymmetric molecular orientation, the orientation of the moleculars in one branch being in the opposite direction to the orientation of the molecules in the other branch. A

method of making such a modulator may compromise the step of heating the structure to a temperature above the glass transition temperature of the polymeric electro-optical material, applying a poling electric field to each waveguide branch, the field on one branch being of the opposite polarity to the field on the other branch, maintaining the field for a sufficient time to ensure that the molecules of the polymer are substantially in the desired orientation, cooling the structure to below the glass transition temperature and then removing the electric field. Reference is made to the drawings, in which:

Figure 1 is a schematic drawing of a polarization-insensitive optical Mach-Zehnder interferometric electro-optic light modulator in accordance with the present invention;

Figures 2 and 3 are schematic plan and sectional views of portions of the device shown in Figure 1, and indicate non-centrosymmetric orientation of organic molecules parallel to the direction of an applied electric field;

Figure 4 is a plan view of an optical modulator

according to a preferred embodiment of the invention;

Figure 5 is an enlarged view of the portion of Figure 4 marked A, drawn with the horizontal scale considerably compressed in comparison with the vertical scale for the sake of clarity; and

Figure 6 is an enlarged section on line BB of Figure 5.

In the modulator represented in Figure 1, the propagation constant of each of the waveguide channels is changed by means of an electric field respectively applied vertically and horizontally to the waveguide channels. The difference in the propagation speed of light in the two channels produces an electrically controlled phase shift. The output light intensity varies with the phase shift, and therefore is modulated by the applied voltage through the electro-optical effect.

The polarization-insensitive character of the light modulation is achieved by balancing the voltages of the two parallel sets of electrodes separately situated on the respective waveguide channels, so as to effect equal

phase modulation of the TE and TM modes with the horizontal and vertical electric fields.

The applied voltage can be AC or DC, and typically will be between about 0-400 volts. The frequency of the applied field will vary between DC and the gigahertz region.

Referring to Figure 1, the modulator 10 consists of a transparent nonlinear optical polymeric film component 11 on a supporting substrate. Film 11 has an input optical waveguide 12 that Y branches at 14 to split a randomly polarized light input 20 between light path channel 22 and light path channel 23. The light propagating along channels 22 and 23 reconverges through Y branches at 15, and exits through waveguide 16 as light output 21. The polymeric medium of the waveguide channels has a higher refractive index than the polymeric film which is contiguous with the waveguide channels, and also higher than the non-linear optically responsive cladding layers 24 (Figure 3) which are utilized as protective layers.

Electrodes 25 are connected to voltage source 27, and are activated to apply a vertical electric field to

channel 22. Electrodes 26 are connected to voltage source 28, and are activated to apply a horizontal electric field to channel 23. The polymeric medium between electrodes 25 in channel 22 has a stable molecular orientation which is parallel to the vertical electric field applied by electrodes 25. The polymeric medium between electrodes 26 in channel 23 has a stable molecular orientation which is parallel to the horizontal electric field applied by electrodes 26.

In an operating mode, the modulator 10 is utilized in combination with a laser radiation source 30 of arbitrary polarization which provides input laser beam 20, and with a photodetector 31 which functions to convert the output signal 21 to a reconstructed electrical signal.

The input coherent electromagnetic radiation preferably is a laser beam, for example of wavelength 800-1500 nm, output by a semiconductor laser.

The organic film-supporting substrate illustrated in Figure 3 can be constructed of any convenient non-conducting medium, such as plastic, glass or silicon.

Referring to Figure 2, channel 23 has a non-centrosymmetric orientation of organic molecules which is parallel to the direction of the field applied by electrodes 26 and generally parallel to the plane of the substrate of the waveguide device.

In Figure 3, substrate 10 is shown as a support layer for the laminated assembly of waveguide layers. Channel 22 and cladding layers 24 have a non-centrosymmetric orientation of organic molecules which is parallel to the direction of the electric field applied by electrodes 25 and generally perpendicular to the plane of the substrate of the waveguide device.

The thin film organic waveguiding medium 22 and the cladding layers 24 are transparent, and either isotropic or liquid crystalline in physical properties, each exhibiting non-linear optical response.

A typical thin film organic medium or cladding layer comprises a blend of a polymer host and a guest component. The non-linear optical properties of the thin film and cladding layers can be controlled by the guest component alone, or both the host and the guest

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components can exhibit non-linear optical susceptibility.

Illustrative of suitable host polymers are poly-(methylmethacrylate), cellulose acetate, polysiloxane, polyacrylamide, polyacrylonitrile, polycarbonate, nylon, polyethylene, polysulfone, polystyrene, and polyurethane.

Illustrative of suitable guest compounds are 4-nitroaniline, 2-methyl-4-nitroaniline, and 4-N,N-dimethylamino-4'-nitrostilbene (DANS).

Other suitable non-linear optically active guest compounds are illustrated by quinodimethane structures corresponding to the formulae:

$$\begin{array}{c} R \\ R \end{array} C = \underbrace{\qquad\qquad}_{n} C \begin{array}{c} R^1 \\ R^1 \end{array}$$
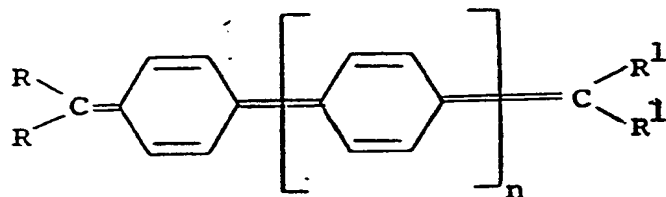
- 13 -
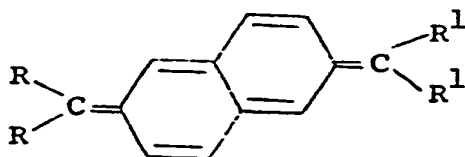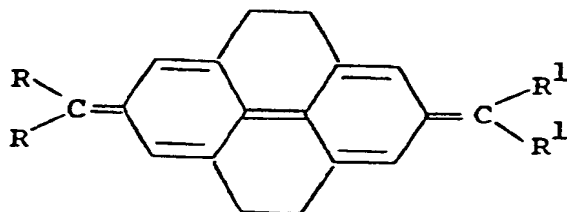
where n is an integer with a value of 0-3; R and R^1 are substituents selected from hydrogen and aliphatic, alicyclic and aromatic groups containing 1-20 carbon atoms, and at least one of the R substituents is an electron-donating group, and at least one of the R^1 substituents is an electron-withdrawing group.

Illustrative of non-linear optically active quino-dimethane species are 7,7-di(n-hexyldecylamino)-

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8,8-dicyanoquinodimethane; 13,13-diamino-14,14- dicyano-diphenoquinodimethane; 13,13-di(dimethylamino)-14,14-di-cyanodiphenoquinodimethane; 13,13-di(n-hexadecylamino)-14,14-dicyanodiphenoquinodimethane; 13,13-ethylenedi-amino-14,14-dicyanodiphenoquinodimethane; 13,13-di-(methylamino)-14,14-dicyano-4,5,9,10-tetrahydropyreno-quinodimethane; and 13,13-di(n-hexadecylamino)-14,14-dicyano-4,5,9,10-tetrahydropyrenoquinodimethane.

The synthesis of quinodimethane compounds as listed above is described in US-A-4 640 800 and US-A-4 707 305.

The term "electron-donating" as employed herein refers to organic substituents which contribute electron density to the pi-electron system when the conjugated electronic structure is polarised by the input of electromagnetic energy, e.g., amino, oxy or thio.

The term "electron-withdrawing" as employed herein refers to electronegative organic substituents which attract electron density from the pi-electron system when the conjugated electron structure is polarized by the input of electromagnetic energy, e.g. nitro, cyano, trifluoromethyl, tricyanovinyl or triflone.

A particular host polymer is selected for ease of fabrication, optical properties, and compatibility with the organic guest component. The guest component typically will constitute between about 5-60 weight percent of a thin film waveguide or cladding guest/host medium.

A polymer which exhibits non-linear optical response can be employed as a host component, or it can be utilised as a sole component. This type of organic component is illustrated by thermoplastic polymers which are characterised by a recurring monomeric unit corresponding to the formula;

$$\begin{array}{c} -\!\!\left[\!\!-\mathrm{P'}\!-\!\right]\!\!- \\ | \\ \mathrm{S'} \\ | \\ \mathrm{M'} \end{array}$$
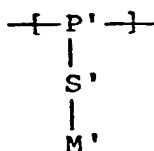
where P' is a polymer main chain unit, S' is a flexible spacer group having a linear chain length of between 1-20 atoms, M' is a pendant group which exhibits a second order non-linear optical susceptibility .., the pendant groups constituting at least 10 weight percent of the polymer, and the polymer having a glass transition temperature above about $40^{\circ}\mathrm{C}$.

Thermoplastic side chain polymers corresponding to the above formula can be either isotropic or liquid crystalline in physical properties. Suitable side chain polymers are described in US-A-4 694 066. Illustrative of side chain polymers are poly [6-(4-nitro-biphenyloxy)hexyl methacrylate], poly (L-N-p-nitro-phenyl-2-piperidinmethyl acrylate), and stilbene-containing polymers such as:

$$-\left[O-CH_2-CH\right]-$$
$$(CH_2)_6-O-\underset{}{\bigodot}-CH=CH-\underset{}{\bigodot}-CN$$

$$-\left[CH_2-\underset{\underset{}{\overset{CH_3}{|}}}{C}\right]--\left[CH_2-\underset{\underset{CO_2-CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]-$$

$$CO_2-(CH_2)_2-\underset{\underset{}{\overset{CH_3}{|}}}{N}-\underset{}{\bigodot}-CH=CH-\underset{}{\bigodot}-NO_2$$
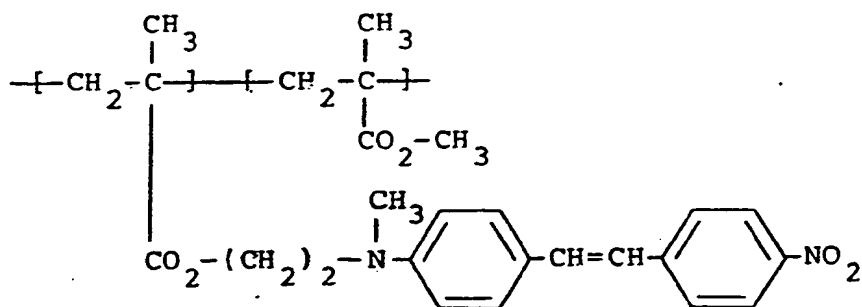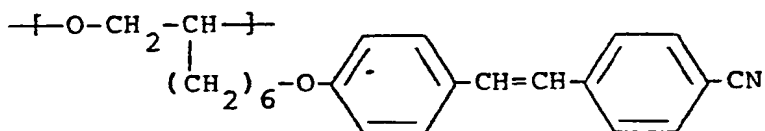
An electro-optic device according to the present invention has waveguide thin film and cladding optical paths which have an external field-induced alignment of molecular dipoles, such as nonlinear optically-active

guest molecules, or nonlinear optically-active pendant side chains of polymers of the type described above.

Poling of the thin film and cladding layers can be accomplished conveniently by heating the assembly to near or above the melting point or glass transition temperature of the organic media, then applying a DC electric field (e.g. 50-150 V/μm) to the organic media to align molecular dipoles in a uniaxial orientation. The assembly then is cooled while the organic strata are still under the influence of the applied DC electric field. In this manner a stable and permanent molecular orientation is immobilized in a rigid structure, such as between the pairs of electrodes shown in Figure 2 and Figure 3.

Electrode pairs 25 and 26 in Figure 1, Figure 2 and Figure 3 can be a strip coating of a suitable conducting material such as aluminium, silver, gold, copper, indium-tin oxide, or indium titanate, and are connected to DC or AC power sources 27 and 28.

The thin film waveguide layer 22 and cladding layers 24 as shown in Figure 3 can be formed on the supporting substrate 10, together with the electrodes,

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by conventional fabricating techniques such as spin coating, spraying, Langmuir-Blodgett deposition, and sputtering, as appropriate for the respective materials.

The following example is further illustrative of the present invention.

EXAMPLE

This example illustrates the construction and operation of a polarization-insensitive waveguide electro-optic modulator in accordance with the present invention as represented in Figure 1.

A commercially available silicon dioxide-coated silicon wafer is placed in a Varian electron beam vacuum deposition system. A 0.1 μm layer of 99.999% purity aluminium is deposited on the wafer.

AZ-1518 positive photoresist (Hoechst) is spin-coated on the aluminium-coated wafer with a Solitec model 5100 coater. A 1.5 μm photoresist coating is achieved by spinning at 5000 rpm for 30 seconds. The photoresist coating is dried in a vacuum oven at 90°C for 30 minutes. The device illustrated is a

Mach-Zehnder optical modulator in which the electro-optic effect is used to vary the speed of light travelling along the waveguides in such a manner that the phase shift between the two waveguides is converted into intensity modulation at the output of the device.

The photoresist coating is patterned in the form of lower electrode 25 in Figure 1 by placing the wafer in contact with a mask of the desired configuration in a Karl Suss model MJB3 mask aligner, and exposing the marked coating to 405 nm radiation (120 mJ/cm^2).

The mask is removed, the patterned photo-resist is developed with AZ-400k Developer in water (1:1) over a period of 45 seconds, and the developing cycle is terminated by washing with deionized water.

The photoresist-coating of the wafer is baked in a vacuum oven at 120°C for 30 minutes. The exposed aluminum pattern is etched with type A etchant for 50°C for 20 seconds, and the etched surface is rinsed with deionised water.

The aluminium electrode surface of the wafer is covered with a thin (100 nm) protective polysiloxane

layer, followed by a 1.5 .m lower organic cladding layer of a 20% solution of a copolymer (40/60) of methyl methacrylate/4-methacryloyloxy-2-ethoxy-4'-nitrostilbene in trichloropropane by spin-coating at 3000 rpm for 30 seconds, and the cladding layer is dried in a vacuum oven at 160°C for one hour. The organic polymer has a molecular weight of about 30,000 and the cladding layer has a refractive index of 1.42.

The wafer then is exposed to reactive ion etching for 5 seconds to improve surface adhesion to subsequent layers. The etching conditions are five standard cubic centimeters per minute of O_2 flowing at 15 mtorr pressure, with 30 watts/6" diameter of 13.56 MHz r.f. power.

A non-linear optically active thin film waveguide layer of 1.65 .m thickness is spin-coated on the lower cladding layer at 3000 rpm. The spin-coating medium is a 20% solution of a copolymer (50/50) of methyl methacrylate / 4- (methylacryloyloxy-2-ethoxy)-4'-nitro-stilbene in trichloropropane. The organic layer is dried in a vacuum oven at 160°C for one hour. The organic polymer has a molecular weight of about 30,000, and the thin film has a refractive index of 1.49.

A photoresist layer of AZ-1518 is spin-coated on the thin film waveguide layer at 4000 rpm, and the layer is exposed to 405 nm radiation (120 mJ/cm^2). A 0.2 μm layer of aluminium is deposited on the photoresist layer. The aluminium layer is coated with a photoresist layer and the layer is patterned in the form of a Mach-Zehnder interferometric waveguide as represented in Figure 1. The waveguide width is 5 .m. The Y junction channels separate and recombine at a full angle of 1.2°.

The upper surface of the waveguide structure is exposed to reactive ion etching for 15 minutes under oxygen plasma conditions as previously described, to remove the multilayers down to the bottom silicon substrate, except for the photoresist coated pattern. The etching cycles also remove the photoresist coating from the aluminium pattern.

The aluminium and lower photoresist layers are removed by immersion of the waveguide structure in AZ-400k developer for one minute.

The substrate and the upper surface multilayer rib pattern are spin-coated with an upper organic cladding

layer in the same manner as described above for the lower cladding layer.

A 0.1 μm layer of aluminium is deposited on the upper organic cladding layer, and following the pattern procedures described above the upper electrode 25 and electrodes 26 in Figure 1 are formed.

The waveguide structure is cleaved at opposite ends to provide two sharp faces to couple light in and out of the waveguiding thin film and cladding assembly.

Molecular orientation of the two polymeric waveguide assembly sections between the two sets of electrodes respectively is accomplished by application of electric fields by the sets of electrodes.

The fabricated waveguide device is placed in a Mettler hot stage, and the unit is raised to 90°C at 1°C/min. A DC field of 70V/μm and an AC voltage of 5 volts sine (10,000 t) is applied to one set of electrodes, and a variable DC voltage and an AC voltage of 5 volts sine (10,000 t) are applied to the other set of electrodes.

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Objective lenses (10X) are employed to focus and couple 1.34 μm radiation (100mW continuous wave) into the Mach-Zehnder Waveguide. The output of the waveguide is passed through a 10X microscope objective, a polarization beam splitter, and then into two optical detectors. The detector signals are transmitted to two lock-in amplifiers.

Both amplifiers are tuned for a signal at 10,000 Hertz, and the variable DC voltage to the first set of electrodes is adjusted until the signals in the two amplifiers are identical.

The waveguide unit is held at 90°C for 20 minutes under the adjusted applied fields, and the applied fields are maintained while the waveguide unit is cooled to room temperature at 1°C/minute.

Referring now to Figures 4 to 6, the device illustrated is a Mach-Zehnder optical modulator in which the electro-optic effect is used to vary the speed of light travelling along the waveguides in such a manner that the phase shift between the two waveguides is converted into intensity modulation at the output of the device.

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The device comprises a substrate 41 on which the waveguide 42 is formed. Electrodes 43 and 44 overlie the branches of the waveguide forming the Mach-Zehnder interferometer structure. Optical fibres 45 and 46 are coupled to the ends of the waveguide 42. The structure of the waveguide will be described hereinafter in more detail with reference to Figure 6.
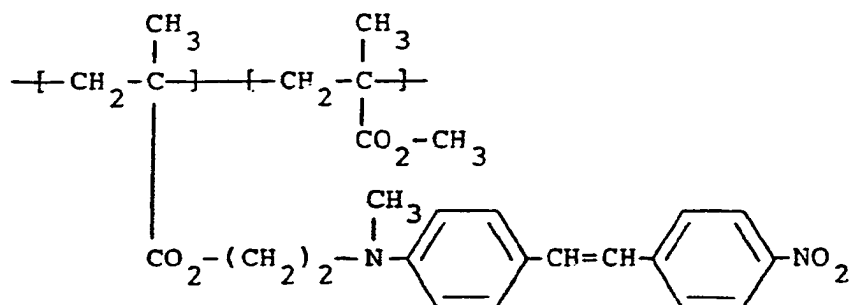
Figure 5 shows the division of the waveguide 42 into two branches 42A and 42B via an elongate Y-section 42C which includes an angle between the arms of the Y junction of about 1.2°.

In use, the modulating r.f. signal is applied equally to each electrode 43 and 44 but since, as hereinafter described, the underlying waveguides are poled in opposite directions, the instantaneous modulation will cause an increase in the refractive index on one branch and a decrease in refractive index on the other branch thereby causing "push-pull" modulation of the amplitude of the light emerging from the opposite end of the modulator.

The construction of the modulator will now be

described with reference to Figure 6. A silicon substrate 50 is plated with a thin layer of gold as a ground plane electrode 51, and which also serves as the counter electrode for poling. If desired, the ground plane electrode 51 may be patterned so as to avoid the upper poling electrode, hereinafter described, directly overlying the lower electrode, which can lead to breakdown between the electrodes. On to the gold electrode 51 a buffer or cladding layer 52 of polymer is spun on. The polymer used is a stilbene containing monomer of the following formula:

$$-[CH_2-\underset{\underset{CO_2-(CH_2)_2-N-}{|}}{\overset{\overset{CH_3}{|}}{C}}]-[CF_2-\underset{\underset{CO_2-CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}]-$$

with the pendant group: $CO_2-(CH_2)_2-N(CH_3)-C_6H_4-CH=CH-C_6H_4-NO_2$

co-polymerised with methyl methacrylate. Two different copolymers are blended together to achieve the desired refractive index, which should be approximately 0.007 lower than that of the waveguiding region, as hereinafter described. The first is a 50:50 copolymer, while the second is a 35:65 copolymer. The copolymers

are dissolved in cyclohexanone to form a 25 to 30 wt.% solution, and the solution is spun onto the gold plated substrated at 1600 rpm for 10 seconds to form the layer 52 of approximately 7 um thick. The substrate is then baked for 6 hours at 165°C and then transferred to an oven at 110°C for 1 hour.

A waveguiding channel pattern is then formed in the cladding layer 52, according to the desired pattern of the waveguide 42, by first evaporating onto the surface of the cladding layer a layer of gold approximately 100 nm thick. A positive photo-resist material is spun onto the gold layer and this layer is exposed in accordance with the desired pattern through a mask. The photo-resist is developed to remove it from the areas where the waveguide is to be defined, and the exposed gold in these areas is removed using a conventional gold etch solution. The remaining photo-resist material is then removed and the material is subjected to oxygen plasma reactive ion etching to achieve a channel depth in the waveguide areas of approximately 2.5 um. The remaining gold is etched off.

A smoothing layer 53 is applied by spinning onto the material a 7 wt.% solution in cyclohexanone of the

copolymer blend used to form the buffer or cladding layer. The material is spun on at 1700 rpm for 10 seconds. The resulting layer 53 is of a thickness just sufficient to provide smoothing of the surface imperfections caused by the reactive ion etching of the channel.

A waveguiding layer 54 is formed next by spinning on a 20 to 25 wt.% solution in cyclohexanone of the 50:50 copolymer hereinbefore described with reference to the buffer or cladding layer so as to achieve a layer thickness away from the channel of 2 μm. The material is then baked for six hours at $165^{\circ}C$ and then for one hour at $110^{\circ}C$.

A top cladding layer 55 is provided over the waveguiding layer by spinning on at 2000 rpm for ten seconds the same solution as used to provide the lower buffer or cladding layer 52. A layer of about 5 μm in thickness is produced. This is baked at $165^{\circ}C$ for approximately eighteen hours followed by one hour at $110^{\circ}C$.

Combined driving and poling electrodes 56 are provided on the upper surface in the pattern illustrated

in Figures 5 and 6 by first evaporating onto the upper surface a layer of gold approximately 100 nm thick. A layer of positive photo-resist is then coated onto the gold to a thickness of approximately 3 μm and is exposed according to the desired pattern through a mask and developed to remove the photo-resist in the electrode areas. Further gold is electroplated through the mask to build up the thickness to 3 μm. The photo-resist is stripped off and gold etch applied to remove the gold from the non-electrode areas.

Poling of the waveguiding channel regions is carried out by heating the device to a temperature of 130°C, which is above the glass transition temperature for the polymer. Voltages are applied to the electrodes 43 and 44 to create fields in opposite directions in the two branches of the waveguide equal to about 200 V/μm, for thirty minutes. With the field still applied, the material is then cooled to beneath the glass transition temperature and the field is removed.

The resulting modulator may be operated at a modulating frequency of about 10 GHz and has a bandwidth of 10 to 20 GHz. The power requirement is low and the drive voltage is approximately 2.5 V.

CLAIMS

1.   An electro-optic waveguide device, comprising a polymeric electro-optic waveguiding region located between upper and lower cladding layers of lower refractive index than the waveguiding region, and electrodes for applying an electric field to the waveguiding region, at least one of the cladding layers being an electro-optic layer.

2.   A device according to Claim 1, wherein both cladding layers are electro-optic layers.

3.   A device according to Claim 1 or 2, wherein one of the cladding layers extends over at least a part of each side of the waveguiding region.

4.   A device according to any preceding claim, wherein the waveguiding region and/or the cladding layers comprises a polymeric host matrix, and an organic guest compound which exhibits second order non-linear optical susceptibility.

5.   A device according to any of claims 1 to 3, wherein

the waveguiding region and/or the cladding layers comprise an organic polymer with pendant side chains which exhibit second order non-linear optical susceptibility.

6. A device according to Claim 5, wherein the waveguiding region is a region having stable electric field induced noncentrosymmetric polymer molecular orientation.

7. A device according to Claim 6, wherein cladding layers have stable electric field-induced zones of noncentrosymmetric polymer molecular orientation.

8. A device according to Claim 5, 6 or 7, wherein the waveguiding region and the cladding layers each comprises a stilbene structure in conjugation with an electron-donating group and an electron-withdrawing group.

9. A device according to Claim 8, wherein the waveguiding region and the cladding layers each comprises an acrylic copolymer with pendant side chains which contain a 4-amino-4'-nitrostilbene structure.

10.   A device according to any preceding claim, wherein the cladding layers each have a refractive index 0.001 to 0.2 lower than the waveguiding region.

11.   A radiofrequency optical modulator comprising an optical waveguide structure arranged as a Mach-Zender interferometer, wherein each branch of the interferometer is formed of a polymeric electro-optic material having a stable electric field-induced noncentrosymmetric molecular orientation, the orientation of the molecules in one branch being in the opposite direction to the orientation of the molecules in the other branch.

12.   A modulator according to claim 11, wherein the interferometer is formed on a substrate and the orientation in each branch is substantially normal to the plane of the substrate.

13.   A method of making a radiofrequency optical modulator as defined in Claim 11 or 12, comprising the step of heating the structure to a temperature above the glass transition temperature of the polymeric electro-optical material, applying a poling electric field to each waveguide branch, the field on one branch

being of the opposite polarity to the field on the other branch, maintaining the field for a sufficient time to ensure that the molecules of the polymer are substantially in the desired orientation, cooling the structure to below the glass transition temperature and then removing the electric field.

14. A waveguide medium for optical modulation which comprises:

a. a waveguide organic thin film component which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$; and

b. an upper cladding layer and a lower cladding layer, each of which consists of a transparent organic medium which has a lower index of refraction than the waveguiding thin film component, and which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$.

15. A waveguide medium in accordance with claim 14, wherein the waveguiding thin film component comprises an organic polymeric host matrix, and an organic guest compound which exhibits second order nonlinear optical susceptibility ..

16. A waveguide medium in accordance with claim 14 wherein each of the cladding layers comprises a polymeric host matrix, and an organic quest compound which exhibits second order nonlinear susceptibility β.

17. A waveguide medium in accordance with claim 14 wherein the waveguide thin film component and the cladding layers each comprises an organic polymer with pendant side chains which exhibit second order nonlinear optical susceptibility. β

18. A thin film waveguide electro-optic light modulator which consists of a laminated assembly of layers comprising:

a. a waveguide thin film of an organic polymer component which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$ and

b. upper and lower cladding layers, each of which consists of an organic polymer medium which has an index of refraction between about 0.001-0.2 lower than the waveguiding thin film component, and which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$ and

electrodes positioned to apply an electric field to the assembly.

19. A thin film waveguide modulator in accordance with claim 18 wherein the thin film component has a waveguiding channel configuration.

20. A thin film waveguide modulator in accordance with claim 18, wherein the thin film component has a channel phase modulation configuration.

21. A thin film waveguide modulator in accordance with claim 18, wherein the thin film component has an interferometric channel waveguide configuration.

22. A thin film waveguide modulator in accordance with claim 18, wherein the laminated assembly of substrates has a polarization-insensitive Mach-Zehnder interferometric waveguiding structure.

23. A thin film waveguide modulator in accordance with claim 18, wherein the thin film component has a two channel directional coupling configuration.

24. A thin film waveguide modulator in accordance with

claim 18, wherein the thin film component has a two channel cross-bar switching configuration.

25. A thin film waveguide modulator in accordance with claim 18, wherein the waveguiding thin film component and the cladding layers each comprise an organic polymer with pendant side chains which confer second order nonlinear optical susceptibility upon the polymer, and wherein the thin film component and cladding layers have stable electric field-induced zones of noncentrosymmetric polymer molecular orientation.

26. A thin film waveguide modulator in accordance with claim 18, wherein the waveguiding thin film component and the cladding layers each comprise an acrylic polymer with pendant side chains which contain a stilbene structure in conjugation with an electron-donating group and an electron-withdrawing group.

27. A thin film waveguide modulator in accordance with claim 18, wherein the waveguide thin film component and the cladding layers each comprises an acrylic copolymer with pendant side chains which contain a 4-amino-4'-nitrostilbene structure.

28. A channel waveguide electro-optic phase modulator comprising:

a. A linear waveguide channel which consists of a laminated assembly of layers comprising:

(1) a waveguide thin film of an organic polymer component which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$;

(2) upper and lower cladding layers, each of which consists of an organic polymer medium which has an index of refraction between about 0.001-0.2 lower than the waveguiding thin film component, and which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$; and

b. electrodes which are positioned to apply an electric field to the waveguide channel.

29. An interferometric waveguide electro-optical modulator comprising:

a. first and second waveguide channels diverging from a common light input to form co-extensive channels of substantially identical optical length, and reconverging

to a common light output, wherein the waveguide channels
are composed of a laminated assembly of layers
comprising:

(1) a waveguide organic thin film component which
exhibits second order nonlinear optical susceptibility
$X^{(2)}$;

(2) an upper organic cladding layer and a lower organic
cladding layer, each of which has a lower index of
refraction than the waveguide thin film component, and
at least one of which exhibits second order nonlinear
optical susceptibility $X^{(2)}$; and

b. a set of spaced electrodes positioned in proximity
along a channel to facilitate the application of an
electric field to the channel organic medium, wherein
the organic medium zone between the spaced electrodes
has a non-centrosymmetric molecular orientation which is
parallel to the direction of an applied electric field.

30. A waveguide electro-optic modulator in accordance
with claim 29, wherein the channel waveguiding thin film
component and the cladding layers each comprise an
organic polymer with pendant side chains which confer

second order nonlinear optical susceptibility . on the polymer.

31. A channel waveguide electro-optic modulator having a directional coupling configuration which comprises:

a. first and second waveguide channels in a parallel and co-extensive proximity, wherein each channel consists of laminated assembly of layers comprising:

(1) a waveguide thin film of an organic polymer component which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$;

(2) upper and lower cladding layers, each of which consists of an organic polymer medium which has an index of refraction between about 0.001-0.2 lower than the waveguiding thin film component, and which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$; and

b. electrodes which are positioned to apply an electrical field to the waveguide channels.

32. a channel waveguide electro-optic modulator having a cross-bar switching configuration which comprises:

a. first and second waveguide channels which intersect to form a junction, wherein each channel consists of a laminated assembly of layers comprising;

(1) a waveguiding thin film of an organic polymer component which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$;

(2) upper and lower cladding layers, each of which consists of an organic polymer medium which has an index of refraction between about 0.001-0.2 lower than the waveguiding thin film component, and which exhibits second order nonlinear optical susceptibility $\chi^{(2)}$; and

b. electrodes which are positioned to apply an electrical field to the channel junction.

33. An electro-optic waveguide device, substantially as described with reference to the drawings.